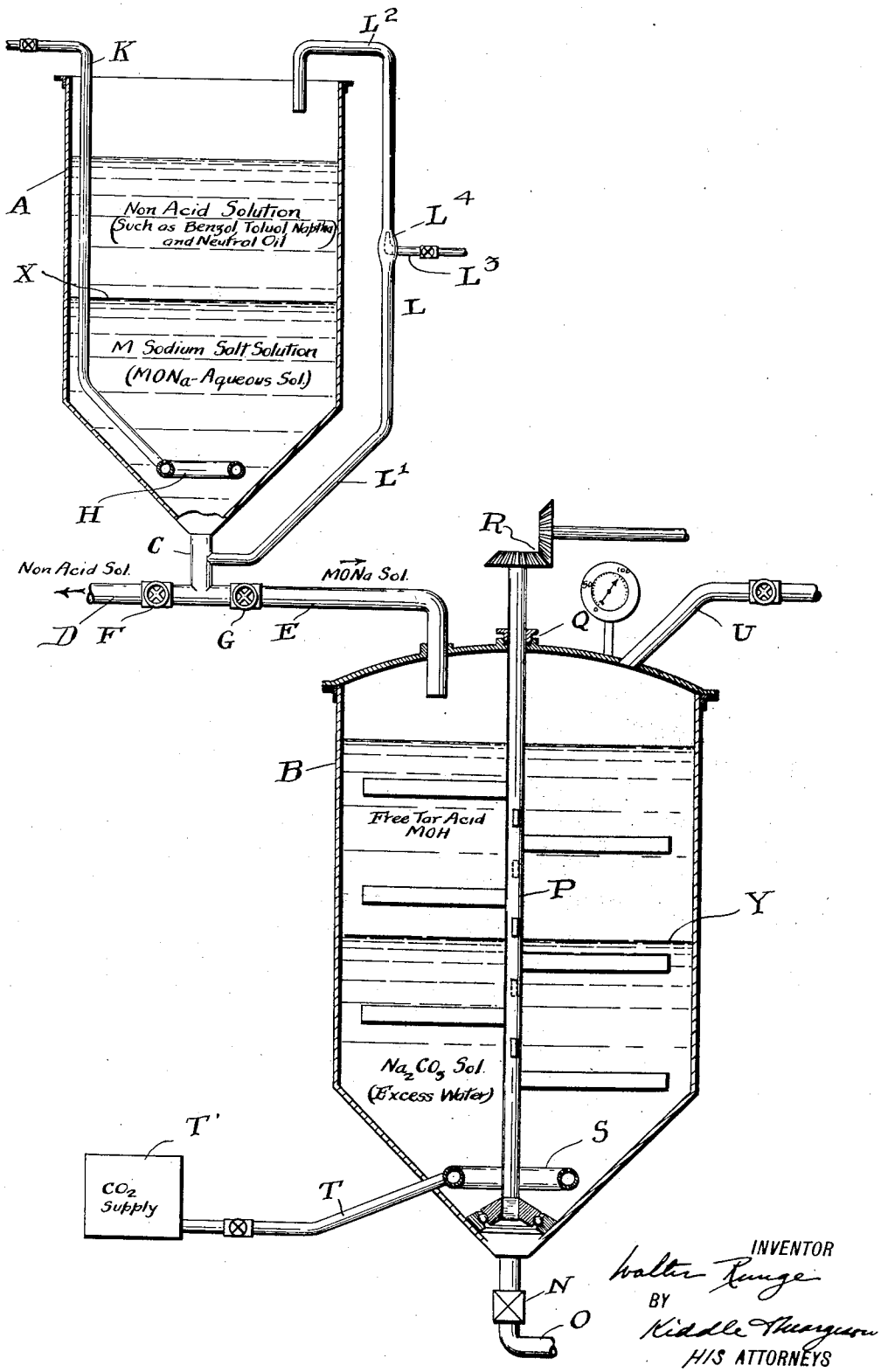
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OBTAINING TAR ACIDS.

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1,409,588.

Patented Mar. 14, 1922.



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OBTAINING TAR ACIDS.

1,409,588. Specification of Letters Patent. Patented Mar. 14, 1922.

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To all whom it may concern:

Be it known that I, WALTER RUNGE, a citizen of the United States, and a resident of Orange, in the county of Essex and State of New Jersey, have made certain new and useful Improvements in Obtaining Tar Acids, of which the following is a specification.

The invention relates to the manufacture or recovery of tar acids, such as phenol, cresylic acid and the higher homologues (higher tar acids).

An object of the invention is to provide a method whereby such tar acids as those referred to can be recovered in a more expeditious manner than by any known method.

Coal tars when successively heated to the following temperatures can, by distillation be divided into various fractions. For example, by carrying out a distillation operation where the maximum temperature is up to 170 degrees C. a light oil fraction is derived; where the maximum temperature is up to 230 degrees C. a middle oil fraction is derived; where the maximum temperature is up to 270 degrees C. a creosote oil fraction is derived, and where the maximum temperature is up to 360 degrees C. an anthracene oil fraction is derived.

These several fractions are, respectively, referred to as the light oil, middle oil, creosote oil and anthracene oil. Each fraction thus obtained contains tar acids and herein applicant is interested only in the light oil and in the middle oil. The light and middle oils each contain the tar acids above enumerated, to wit, phenol, cresylic acid and the higher homologues, and which it is the purpose of the present process to quickly and cheaply obtain. Said light and middle oils also contain certain hydrocarbon oils.

According to the process herein described the light and the middle oils can each be treated separately, or they can be treated together, dependent upon whether the hydrocarbon oils of each fraction are to remain separate and thus be recovered separately, or whether the hydrocarbon oils of both fractions may be mixed and as thus mixed together be recovered.

The light oil, that is the light oil fraction, and the middle oil, that is the middle oil fraction, contain several different oils some of which prominent oils are as follows:

Light oil.	*Middle oil.*
Benzol,	Solvent naphtha,
Toluol,	Heavy naphtha,
Solvent naphtha,	Neutral oil,
Phenol, and	Phenol,
Higher tar acids.	Cresylic acid, and
	Higher tar acids.

As previously indicated the present invention is particularly directed to the separating of the tar acids, such as phenol, cresylic acid and the higher tar acids from the hydrocarbon oils, to wit from the benzol, toluol, solvent naphtha, heavy naphtha, and neutral oil.

This separation is accomplished in the manner hereinafter described and may be performed in an apparatus which is illustrated diagrammatically in the sole figure of the accompanying drawing. The phenol, cresylic acid and higher tar acids may be referred to as the M acids or the tar acids and may be designated by the symbol MOH, in which the M represents the base element of the tar acids, such as in the case of phenol, where M would represent the radical C_6H_5—, or in the case of cresylic acid where M would represent the radical $C_6H_4.CH_3$—, and so on for the higher tar acids. In case of mixtures containing a plurality of acids then M represents the base of each acid as, for example, C_6H_5—; $C_6H_4.CH_3$— which represent the bases where the mixture had phenol and cresylic acid. The constituents of the light oil group and of the middle oil group collectively may be broadly referred to as the aromatic derivatives divisable into acid solutions which are the M acids and non-acid solutions. The M or tar acid solution includes, as just indicated, the phenol, cresylic acid and higher tar acids, while the non-acid solution includes benzol, toluol, solvent naphtha, heavy naphtha and neutral oils.

In the performing of the invention the mixture of acid and non-acid solutions is heated with an aqueous solution of caustic soda (NaOH) with the result as follows: The M or tar acids react with the caustic

soda to form the sodium salt of the M or tar acids, as is shown by the following equation:

$$\underset{\text{(The M or tar acids)}}{MOH} + \underset{\text{(aqueous solution of caustic soda)}}{NaOH} + H_2O = \underset{\text{(sodium salt of tar acid)}}{MONa} + \underset{\text{(excess water)}}{H_2O}$$

As an aqueous solution of caustic soda is used the water of the solution will act as a solvent for and will hold the resulting sodium salt in solution.

It will be noted that during this treatment the non-acids are present but are not acted upon by the caustic soda solution and remain inactive and hence have not been included in the equation above.

The operation just referred to is carried out in a tank (an agitator) with agitation for a peroid of 2 to 6 hours and by this agitation the M or tar acids are brought into intimate contact with the caustic soda in the solution to assist the reaction. At the end of this period the agitation is arrested and the contents of the tank allowed to settle. The solution of the sodium salts of the tar acids, being of higher gravity than the non-acid solution, settles to the bottom and the non-acid solution rises. There is a sharp line of demarkation or division where the two solutions meet and due to this physical characteristic of the two solutions they may be separated mechanically. This mechanical separation may be effected as by drawing off the solution of the sodium salt of the M or tar acids; in other words, the M or tar acid sodium salt solution may be separated mechanically by this drawing off operation from the non-acid solution. The M or tar acid sodium salt solution is now treated by bringing into contact therewith and while under pressure carbondioxide CO_2, either as pure CO_2, or as the CO_2 containing any mixed gases as, for example, flue gases. The CO_2 gas is preferably brought into intimate contact, as by bubbling, that is by blowing jets of CO_2 in the aqueous solution containing the sodium salt of the M or tar acids (the MONa.)

The reaction which takes place is as follows:

$$\underset{\text{(sodium salt of M or tar acid in solution)}}{2MONa} + \underset{\text{(carbondioxide)}}{CO_2} + \underset{\text{(water)}}{H_2O} = \underset{\text{(free tar acid) (light liquid)}}{2MOH} + \underset{\text{(sodium carbonate in solution in excess } H_2O\text{) (heavy liquid)}}{Na_2CO_3}$$

(carbonic acid)

The solution of sodium salt of M or tar acids is under substantially super-atmospheric pressure, preferably of 100 pounds, during the time the reaction just described is taking place. Other methods than bubbling for bringing the CO_2 gas into intimate contact with the M or tar acid sodium salt solution may be employed.

It will be understood, however, that an important feature of the present invention is the employment of said pressure which expedites the ultimate reaction. During the process the pressure is maintained substantially super-atmospheric, preferably at 100 pounds, by supplying additional CO_2 under pressure to replace the CO_2 absorbed as the reaction progresses. If CO_2 is supplied by the introduction of flue gas the inert gases that necessarily constitute a part of flue gas are left and collect in the chamber as the reaction progresses. These inert gases that collect are withdrawn as desired, or when they become too great in volume. As the M or free tar acids (MOH) are relatively light or of low specific gravity and as the aqueous solution of sodium carbonate is heavy or of high specific gravity the M or tar acids will be readily separated from the aqueous sodium carbonate solution. It will, therefore, be seen that the sodium carbonate solution separates, due to gravity, from the M or tar acids, thus facilitating mechanical separation.

Referring to the drawing, it will be seen that therein there is illustrated diagrammatically a form of apparatus which can be employed in the realizing of the invention.

In this apparatus there are shown connected tanks A and B respectively, the latter of which is constructed so that substantially super-atmospheric pressure can be maintained while the operation therein is being carried out.

The tank A has an outlet pipe C provided with valve controlled pipes D and E extending in opposite directions. The pipe D is controlled by a hand-valve F while the pipe E is controlled by a hand-valve G. The tank A has in the lower portion thereof a perforated pipe or coil H to which compressed air is supplied by the valve controlled pipe K. The perforated pipe or coil H is a part of the mechanism employed to effect an agitation of the liquid contents of the tank when it is desired that the agitation be carried out. This mechanism in fact provides air agitation, as it is known in the arts, and may be referred to as air agitating means. With the valves F and G closed there is first placed in the tank A the required aqueous solution of caustic soda (NaOH) and this is followed by the insertion of the proper quantity of light oil, or middle oil, or both of these oils, dependent upon whether the light oil, the middle oil or both of the oils is or are to be treated and until agitation is actually started the aqueous solution of caustic soda will remain at

the bottom and the oil or oils will float on the top of this aqueous solution. Whether or not the light oil or the middle oil, or both of these oils is or are introduced is dependent upon the source from which the ultimate M or tar acids are to be obtained. The oils and the solution in the tank are subjected to agitation by the air agitating means just described; they are also preferably heated as will hereinafter appear. As the reaction proceeds there is a tendency for heavy particles in the solution to settle to the bottom of the tank and therefore there is provided a pumping mechanism L in the form of an ejector having a suction pipe L′ extending from the lower portion of the tank and a delivery pipe L^2 emptying into the upper portion of the tank. As the pumping mechanism L is in the form of an ejector dependent for its operation upon steam flowing inwardly through the valve controlled pipe L^3 and being delivered from the nozzle L^4 of the ejector, said ejector can be employed to perform two functions: (*a*) to serve purely as a pump to convey or transfer the contents from the lower portion of the tank to the upper portion of the tank and (*b*) to serve as a means to supply heat during the period the reaction is taking place. It is desirable to maintain the solution hot while the reaction is taking place and it will be manifest that the ejector supplies this heat from the incoming steam. However, heat can be supplied in other ways, as by inserting an independent heating coil in the lower portion of the tank, or by providing a heating means exterior of the tank. Or, the heat could be supplied by air heated prior to passing through and from the coil H. In place of the ejector there could be employed a purely mechanical pump. The pump or ejector L assists in the agitation, as is obvious, due to the transferring of the solution from the lower portion of the tank to the upper portion thereof. The reaction which takes place in this tank generally requires from 2 to 6 hours. When the reaction is completed the contents of the tank are comprised of the non-acid solution which is relatively light and the sodium salt solution of the M or tar acids which is relatively heavy, the latter of which is marked on the drawing MONa. When the settling operation is completed a sharp line of demarkation exists, at X, between the non-acid solution and the MONa solution.

With no pressure in the tank B—viz. with no pressure substantially above that of the atmosphere—the MONa solution can be permitted to flow directly into the tank B by merely opening the valve G and in this way the mechanical separation of the MONa solution from the non-acid solution is completed. When the MONa solution is completely withdrawn the valve G is closed and thereafter by opening the valve F the non-acid solution can be withdrawn from the tank A.

The tank B has an outlet pipe O controlled by a hand-valve N. Within the tank B there is a mechanical agitator P having a shaft extending through a packing Q and suitably driven as by bevel gearing R. In the lower portion of the tank B there is a perforated pipe or coil S to which CO_2 is supplied through a valve controlled pipe T. From the upper portion of the tank there extends a valve controlled pipe U. No substantial pressure exists in the tank B, as will hereinafter appear, when MONa is being supplied to the tank through pipe E. The MONa solution, as has been previously pointed out, is an aqueous solution. When the reaction is being carried out in tank B the CO_2 is supplied under substantially super-atmospheric pressure, as by the compressor T′ through pipe T to the perforated pipe or coil S. As the valve G in pipe E and valve in pipe U are closed during the time the reaction is taking place the CO_2 is supplied in such a manner that the pressure within the tank is maintained at approximately 100 pounds per square inch. The packing Q is constructed so that said pressure can be maintained.

As has been previously pointed out the water of the solution and the CO_2 unite to form carbonic acid which in turn reacts with the MONa and thus there is a continuous absorption of the CO_2 tending to reduce the pressure within the tank B. Therefore, CO_2 must be supplied either continuously or intermittently to replace the CO_2 used up by the reaction. The absorption of the CO_2 tends to reduce the pressure and the CO_2 is supplied not only to furnish the requisite CO_2 necessary for the chemical reaction but also to maintain the desired approximate 100 pounds pressure—substantially super-atmospheric pressure—which expedites the reaction. During the time the reaction is taking place the agitator P is operating and as the CO_2 is introduced under substantially super-atmospheric pressure through the perforated pipe or coil S it will be observed the CO_2 is "bubbled" into the solution being treated within the tank B. The mechanical agitating and the bubbling—which is also agitating—bring the CO_2 into intimate contact with the MONa salt in the solution and with the pressure maintained substantially super-atmospheric the reaction within the tank B is effected in a relatively short space of time. If the CO_2 supplied is derived from flue gases pumped under pressure into the tank B there will be a collection of inert gases in the upper portion of the tank B. These inert gases can

be withdrawn intermittently or continuously by opening the valve in the pipe U. When the reaction is completed the CO_2 supply is shut off, the agitator P is stopped, and the contents of the tank B are allowed to come to rest and settle. The M or tar acids (MOH) which have been freed as the result of the reaction are relatively light and they collect in the upper portion of the tank. The sodium carbonate (Na_2CO_3) which is absorbed in the water of the solution together form what may be called the sodium carbonate solution and this solution being relatively heavy settles or collects in the lower portion of the tank B. When the settling is completed there is a sharp line of demarkation indicated by the line Y between the M or tar acids and the sodium carbonate solution. By opening the valve N the sodium carbonate solution is first withdrawn from the tank B; subsequently the M or tar acids can be withdrawn. In this manner the complete mechanical separation of the sodium carbonate solution and the M or tar acids can be readily effected and the M or tar acids recovered. The valve N is left open until the pressure within the tank B is reduced whereby a new supply of the MONa salt can be introduced into the tank B for treatment and the cycle of operations just described repeated.

As previously indicated an important feature of the present invention resides in the maintaining of the MONa solution under substantially super-atmospheric pressure while it is being treated with CO_2, but it will be pointed out that the expression "maintained at substantially super-atmospheric pressure" as employed herein is not to be construed as necessarily meaning that the pressure must be maintained at some definite amount as, for example, 100 pounds throughout the entire time reaction is taking place, but it is to be broadly construed as covering a situation wherein the pressure may vary somewhat during the reaction but one in which the pressure is maintained at all times substantially super-atmospheric.

It will here be stated that the separation of the tar acids (MOH) from the MONa salts can be accomplished or effected by the CO_2 treatment herein described—that is with a treatment wherein substantially super-atmospheric pressure is employed—in approximately 4 hours; whereas without the employment of substantially super-atmospheric pressure—that is where the reaction is carried out under normal atmospheric conditions or thereabouts—and with a process which employs a scrubbing tower or agitator as an instrumentality to assist or accomplish the required reaction the time required to accomplish said reaction is often as long as 24 hours or even longer.

According to my process the MOH acids can be recovered or reclaimed—separated from the rest of the ingredients of a tar fraction or tar fractions as the case may be—in much less time than by any process heretofore known or employed.

The improvements herein set forth are not limited to the mode of operation, or to the process, construction and arrangement shown and described for they may be employed in various ways, forms and modifications without departing from the spirit and scope of the invention.

What I claim is:

1. The obtaining of a tar acid from its salt by the method which consists in intimately bringing into contact with each other carbon dioxide and said salt while in the presence of water and under a substantially super-atmospheric pressure approximating 100 pounds per square inch, which super-atmospheric pressure is maintained until there results free tar acid, and subsequently separating said free tar acid from the rest of the solution.

2. The obtaining of tar acids from their salt by the method which consists in intimately bring into contact with each other flue gas and said salt while in the presence of water and under a maintained pressure approaching 100 pounds per square inch until the tar acids are liberated, and subsequently separating said tar acids from the rest of the solution.

3. In the obtaining of tar acids the method which consists in subjecting an aqueous solution of sodium salt of tar acids, when under approximately 100 pounds pressure per square inch in a closed receptacle, to the bubbling action of CO_2 until tar acids are freed, and subsequently separating said tar acids from the rest of the solution.

4. In the obtaining of tar acids the method which consists in subjecting an aqueous solution of sodium salt of tar acids, when under a maintained pressure in a closed receptacle and which pressure approximates 100 pounds per square inch, to the bubbling action of flue gas until there result tar acids in free form, and subsequently separating tar acids when in said free form from the rest of the solution, the inert gases which collect at the top of the receptacle being withdrawn therefrom as desired.

This specification signed and witnessed this 7th day of February, A. D. 1918.

WALTER RUNGE.

Signed in the presence of:

EDWIN A. PACKARD,

G. MCGRANN.